



## Amended Specification

Title: Programmable Metallization Cell Memory with  
Multiple Extra-Small Resistive elements

Cross-reference to related applications: This application  
claims the benefit of PPA # 60/394,139, filed by 07/05/2002  
by the present inventor

Federally sponsored research: none

### FIELD OF THE INVENTION

001 The present invention relates generally to the  
structure of programming metallization cell memory (PMCm)  
and its fabrication

### THE BACKGROUND OF THE INVENTION

002 The PMCm is a kind of non-volatile memory using  
programmable metallization cell (PCM) to store the  
information (US Patent No. 6,348,365). A PCM comprises a  
solid electrolyte and a metal elements contacting to a pair  
of electrodes. The metallic ions from the metal layer can

enter the solid electrolyte resistive element under the certain electric field produced by the programming pulse current or voltage. It results in a change of the resistance of the solid electrolyte element and realizes the information storage. Solid electrolyte element is a key part in PMCM and determines the resistance of the memory. To make solid electrolyte element, an opening is normally first formed in a proper layer, usually a dielectric layer. Then the solid electrolyte is filled in the opening. After that, a thin metallic layer is formed on the solid electrolyte resistive element. Bigger the solid electrolyte resistive element, higher the programming energy is needed for the information storage.

003 To reduce the programming energy of the memory, it is desired that the size of the solid electrolyte element be as small as possible. The advantage of reducing element size is not only the decrease of the programming energy, but also that making much faster and higher density memory becomes possible.

004 It is well known that when two unmixable materials are co-deposited onto a substrate, they normally form a composite-phase thin film with two separated phases

containing each material. Herein that the two materials are unmixable means that these two materials are not soluble to each other and do not form an alloy containing these materials. In some cases, one material may form the extra-small particles embedded in another material, such as in the case of Fe/SiO<sub>2</sub> composite thin film (J. Applied Physics, Vol **84**, 1998, p5693). Herein we call this particle as nano-dot particle because it has a size in the order of nanometer ( $1\text{ nm}=10^{-9}\text{ m}=10\text{ \AA}$ ). In the present invention, we use this technique to fabricate PMCM memory with multiple extra-small solid electrolyte element. The method of present invention is relatively simple and low-cost to make ultra small memory elements due to avoiding some complicated photolithography processes.

#### SUMMARY OF THE INVENTION

005     An object of the present invention is to provide a new PMCM memory structure with extremely small solid electrolyte elements. It is also an object of the present invention to provide some methods to make this memory structure. The extremely small size of the solid electrolyte element makes this memory have a good scalability and possibility to make high density memory.

## BRIEF DESCRIPTION OF THE DRAWINGS

**FIG. 1** is a cross sectional view of PMCM memory with multiple solid electrolyte elements.

**FIG. 2** is a simplified and enlarged perspective view illustrating the structure of composite-phase thin film.

**FIG. 3** is a cross sectional view illustrating bottom electrode and composite-phase layer after the nano-dot particles were etched away. An opening was formed after the particle was etched.

**FIG. 4** is a cross sectional view illustrating the memory structure after solid electrolyte material was filled in the opening.

**FIG. 5** shows ion mill process with ion beam perpendicular to layer surface to form a recession of solid electrolyte element from the matrix layer surface.

**FIG. 6** is a cross sectional view illustrating a PMCM memory cell with lamination of resistive element, metal and conductive layers.

#### DETAILED DESCRIPTION OF THE INVENTION

006 **FIG. 1** is a cross sectional view of PMCM memory with multiple solid electrolyte elements. Basically, the memory element comprises of 4 layers: bottom electrode layers **20**, upper electrode layer **40**, resistive layer **30** and metallic layer **37**. The resistive layer **30** is a layer where some solid electrolyte elements **36** with size of about 1 nm to several tens nm ( $1\text{ nm}=10^{-9}\text{ m}$ ) embedded uniformly in a high resistance matrix **32**. The electrode layers **20** and **40** are made of conductive material. The whole memory cell is located between the address lines **10** and **50**.

007 The solid electrolyte elements **36** are made by filling the solid electrolyte material into the openings of the resistive layer **30**. To make the openings, a composite-phase thin film is first deposited on the bottom electrode layer **20**. The composite-phase thin film is a layer where one phase forms the ultra-small particles **31** and embedded uniformly in another phase which forms a matrix layer **32**,

as shown in **FIG. 2**. The thickness of composite-phase layer is in the range of about 1 nm to 100 nm.

008     The selection of the materials for the composite-phase thin film layer should meet following requirements:

(a) the matrix layer material should be selected from a group of high resistive material so that programming current can mainly flow through the resistive elements; (b) the nano-dot particle material and matrix material are not mixable. It means that they are not soluble to each other and don't form an alloy when they come together by some means such as co-deposition of these two materials onto a substrate; (c) nano-dot particle and high resistive matrix materials are chosen such that nano-dot particle is active chemically, while the high resistive matrix material is inactive chemically to some chemical or chemical solution. So the nano-dot particle can be etched away by the selected chemicals in the later process.

009     It is easy to find the materials meeting the above requirements. The oxide, nitride, boride, carbide, boron, silicon, carbon, carboxynitride or the mixture of some of these materials are the good candidates for high resistive matrix material; while most metals and alloys are the good

candidates for the nano-dot particle material. For example, Fe/SiO<sub>2</sub> is a good combination of these materials. Fe is conductive material, while SiO<sub>2</sub> is a high resistive material. Fe and SiO<sub>2</sub> are not mixable. When Fe and SiO<sub>2</sub> were co-deposited onto a substrate by some means such as sputtering, Fe forms very small particles which are uniformly embedded in the SiO<sub>2</sub> matrix layer under the certain deposition conditions. The SiO<sub>2</sub> is a very stable compound to most of chemicals such as acids, e.g. HCl, while Fe is active to most of acids, e.g. HCl. Since the Fe is active to HCl, while the SiO<sub>2</sub> is inactive to HCl, so the HCl is a suitable chemical solution to etch Fe particle and form an opening in SiO<sub>2</sub> matrix layer.

010 The size of the nano-dot particle is defined herein as the diameter of the particles, or their "characteristic dimension" which is equivalent to the diameter where the particles are not cylindrically shaped. The nano-dot particle size is about 1 nm to several tens nm, and more preferably of 3 nm to 50 nm.

011 The composite-phase layer with nano-dot particles can be made by various thin film deposition methods such as sputtering, laser ablation, evaporation, or the chemical

vapor deposition (CVD). The preferred and simple method is to co-sputter a composite target containing these two materials by the magnetron sputtering, RF sputtering or ion beam sputtering. By optimizing the deposition conditions and selecting suitable materials, a well-defined nano-dot particle **31** with desired size can be formed and embedded uniformly in the high resistive matrix layer **32**. To ensure the nano-dot particles are isolated by matrix material, the volume ratio of nano-dot material and matrix material in composite-phase layer should be less than about 3/1, typically, in the range of about 1/1~1/100.

012 After forming the composite-phase layer, the nano-dot particles **31** are etched by choosing suitable chemicals. The etching process can be wet etching or dry etching. The dry etching means that the particles are etched by the plasma of some chemicals. The etching process doesn't etch the matrix. So after the particle was etched away completely, an opening **34** is formed and has the size and shape close to the particle **31**, as shown in **FIG. 3**. After the nano-dot particles **31** are etched, the surface of the bottom electrode **20** is exposed so that the solid electrolyte elements **36** can form a good electrical contact with the electrode **20** after it is filled in the opening **34**.



013     After forming the opening **34** in the resistive layer **30**, the electrolyte material is filled in the openings, as shown in **FIG. 4**. A recession of the electrolyte resistive element **36** from the surface of the matrix or resistive layer may be desired and can be realized by ion mill with ion beam perpendicular to the matrix surface. Most high resistive materials such as oxide, nitride has much smaller etching rate than the most electrolyte materials. So after ion mill, a recession will be formed for electrolyte resistive element and is shown in **FIG. 5**. After forming electrolyte element **30**, a thin layer of metal **37** and upper electrode **40** are deposited on the resistive element layer **30**, as shown in **FIG. 1**.

014     The solid electrolyte layer **30** can also be made by direct co-deposition of a solid electrolyte material and a dielectric material. The solid electrolyte and dielectric should be selected such that they are not mixable when co-deposited together. In such a case, the solid electrolyte material may form small cylinder embedded in the dielectric material in some deposition conditions.

015      The resistance of the memory element can be changed by using a lamination of resistive layer and conductive layer. A PMCM structure with lamination of resistive layer and conductive layer is shown in **FIG. 6**. The advantages of laminated PMCM are improved uniformity of the resistance of each memory and to obtain a desired resistance value by selecting certain lamination number.